

What is claimed is:

1. A composite polymer electrolyte for a lithium secondary battery, which comprises:

5 a composite film structure comprising a first porous polymer film with micro-scale morphology and a second porous polymer film with submicro-scale morphology coated on a surface of the first porous polymer film; and an electrolyte solution impregnated into the composite film structure.

10 2. The composite polymer electrolyte of claim 1, wherein the first porous polymer film is made of polyethylene, polypropylene, polyimide, polysulfone, polyurethane, polyvinylchloride, cellulose, nylon, polyacrylonitrile, polyvinylidene fluoride, polytetrafluoroethylene, a copolymer or blend thereof.

15 3. The composite polymer electrolyte of claim 1, wherein the second porous polymer film is made of a vinylidene fluoride based polymer, an acrylate based polymer, a copolymer or blend thereof.

20 4. The composite polymer electrolyte of claim 3, wherein the second porous polymer film is made of a copolymer of vinylidene fluoride and hexafluoropropylene, a copolymer of vinylidene fluoride and trifluoroethylene, a copolymer of vinylidene fluoride and tetrafluoroethylene, polymethylacrylate, polyethylacrylate, polymethylmethacrylate, polyethylmethacrylate, polybutylacrylate, polybutylmethacrylate, polyvinylacetate, polyethylene oxide, polypropylene oxide, a copolymer or blend thereof.

25 5. The composite polymer electrolyte of claim 1, wherein the first porous polymer film has a thickness of 10 to 25 μm and the second porous polymer film has a thickness of 0.5 to 10 μm .

30 6. The composite polymer electrolyte of claim 1, wherein the second porous polymer film comprises an inorganic material.

7. The composite polymer electrolyte of claim 6, wherein the inorganic material is selected from the group consisting of silica, talc, alumina (Al_2O_3), γ - LiAlO_2 , TiO_2 , and zeolite.

5 8. The composite polymer electrolyte of claim 6, wherein the inorganic material is added in an amount of 1 to 100% by weight, based on the total weight of the polymer of the second porous polymer film.

10 9. The composite polymer electrolyte of claim 1, wherein the electrolyte solution is made of ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, methylethyl carbonate, tetrahydrofuran, 2-methyltetrahydrofuran, dimethoxyethane, methyl formate, ethyl formate, gamma-butyrolactone, or a mixture thereof.

15 10. The composite polymer electrolyte of claim 1, wherein the electrolyte solution is impregnated in the composite film structure in an amount of 1 to 1,000% by weight, based on the total weight of the polymer of the composite film structure.

20 11. The composite polymer electrolyte of claim 1, wherein the electrolyte solution comprises at least one lithium salt selected from the group consisting of lithium perchlorate (LiClO_4), lithium triflate (LiCF_3SO_3), lithium hexafluorophosphate (LiPF_6), lithium tetrafluoroborate (LiBF_4), and lithium trifluoromethanesulfonylimide ($\text{LiN}(\text{CF}_3\text{SO}_2)_2$).

25 12. The composite polymer electrolyte of claim 11, wherein the lithium salt is dissolved in the electrolyte solution in an amount of 1 to 200% by weight, based on the total weight of the polymer of the composite film structure.

30 13. A method of manufacturing a composite polymer electrolyte for a lithium secondary battery, the method comprising:

preparing a first porous polymer film with micro-scale morphology;
uniformly dissolving a microporous polymer with submicro-scale morphology and an inorganic material in a co-solvent in a predetermined ratio to produce a solution;

forming a second porous polymer film by coating the first porous polymer film with the solution to produce a composite film structure which comprises the first porous polymer film and the second porous polymer film that are different in morphologies; and

5 impregnating the composite film structure with an electrolyte solution.

14. The method of claim 13, wherein the co-solvent is selected from the group consisting of acetone, dimethylformamide, dimethylsulfoxide, N-methylpyrrolidone, and a mixture thereof.

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